PEOPLE ADVANCING SCIENCE

PFAS and UCMR 5 Overview

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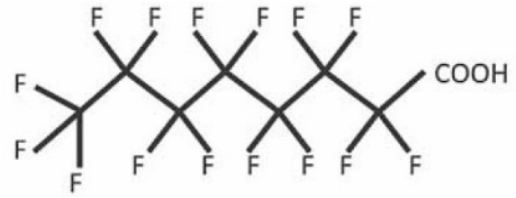
Overview

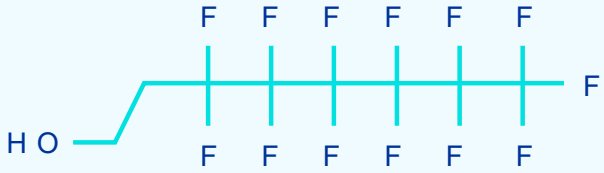
- PFAS Chemistry Overview
- Regulatory Context-HA and Roadmap
- UCMR 5-Methods
- Sampling Guide
- Q&A

CLASSES OF PFAS-Per and Polyfluorinated Alkyl Substances



PERFLUOROALKYL

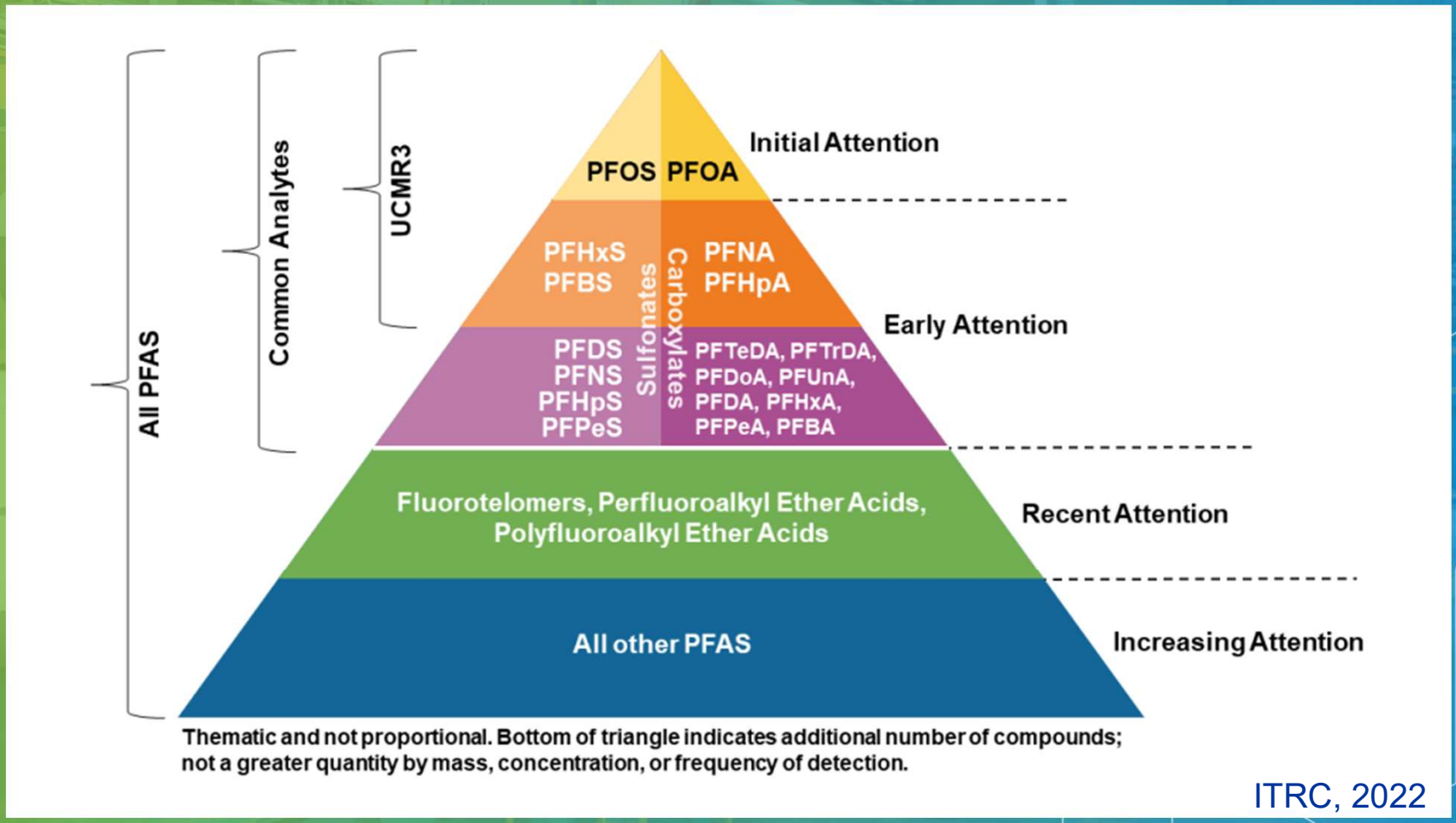
- All hydrogens on the carbons are replaced by fluorine
- Strongest chemical bond in nature
- Difficult to treat
- PFCAs and PFSAs



POLYFLUOROALKYL

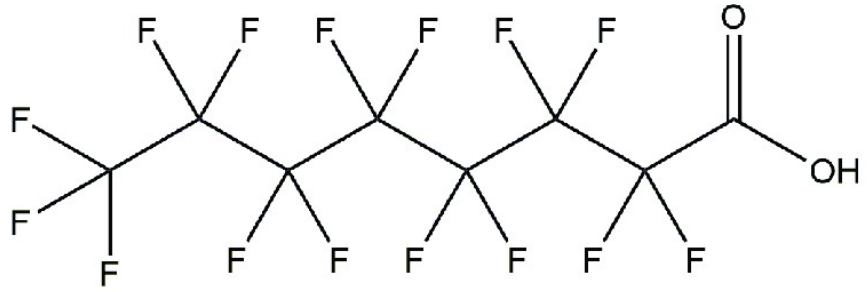
- Non-fluorine atom (usually H or O) attached to at least one, but not all, carbon atoms in the tail
- Creates a “weak link” susceptible to biotic or abiotic degradation
- More susceptible to treatment
- Fluorotelomers
- AKA precursors

Which target compounds to focus on?

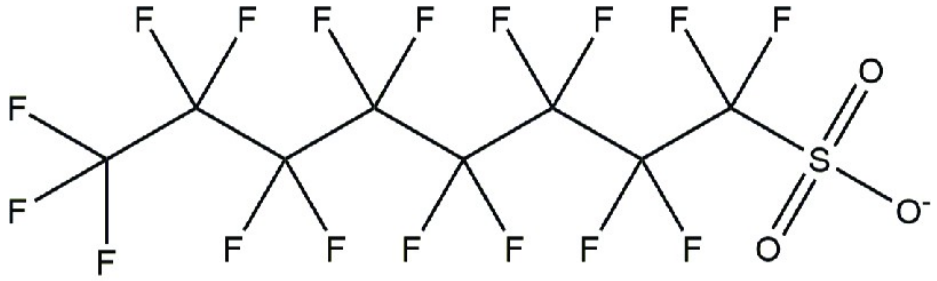


ITRC, 2022

The Two Most Widely Study PFOA and PFOS



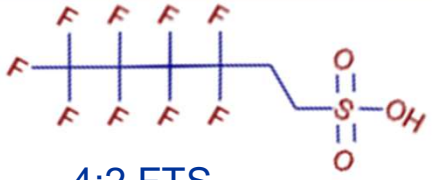
Perfluorooctanoic acid (PFOA)



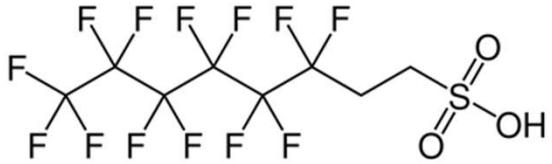
Perfluorooctane sulfonate (PFOS)

- Let's Talk about Bonding C-F
- Who made them?
- What are their uses?
- Why they are so good at what they are made for?
- Known Adverse Health effects.

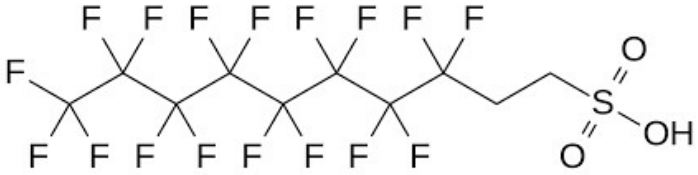
Polyfluorinated PFAS



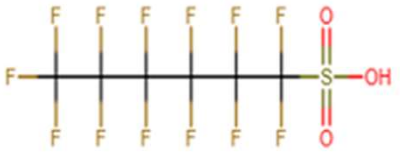
4:2 FTS



6:2 FTS (C8)

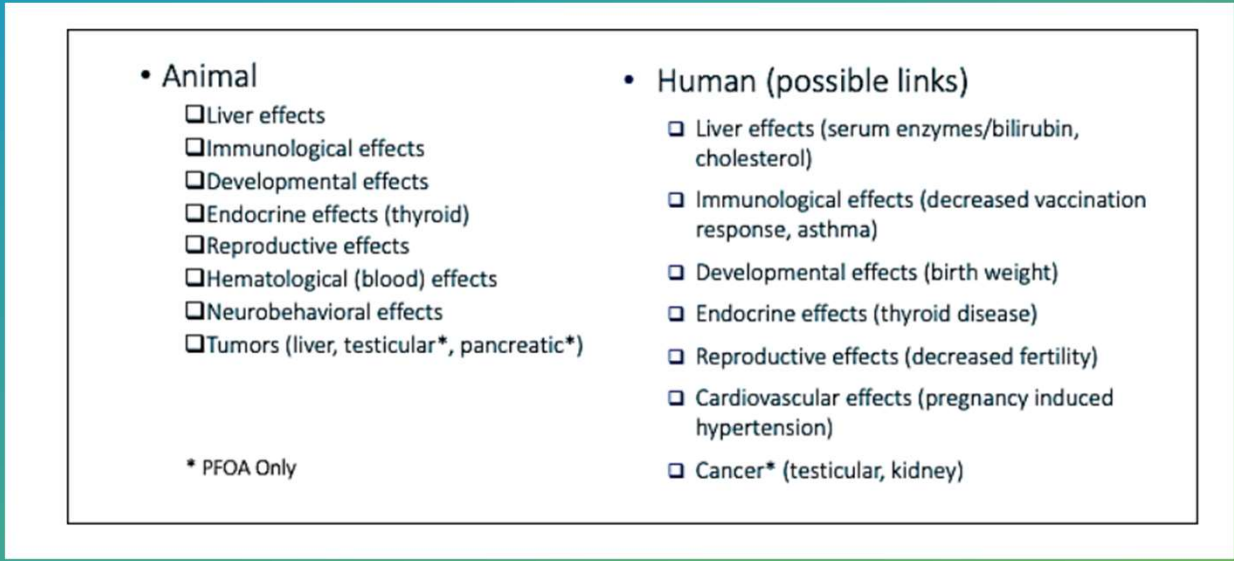


8:2 FTS



Adverse Health Effects of PFAS-PFOA and PFOS

ITRC (Interstate and Regulatory Technology Council) List



- Animal
  - ❑ Liver effects
  - ❑ Immunological effects
  - ❑ Developmental effects
  - ❑ Endocrine effects (thyroid)
  - ❑ Reproductive effects
  - ❑ Hematological (blood) effects
  - ❑ Neurobehavioral effects
  - ❑ Tumors (liver, testicular*, pancreatic*)

* PFOA Only

- Human (possible links)
  - ❑ Liver effects (serum enzymes/bilirubin, cholesterol)
  - ❑ Immunological effects (decreased vaccination response, asthma)
  - ❑ Developmental effects (birth weight)
  - ❑ Endocrine effects (thyroid disease)
  - ❑ Reproductive effects (decreased fertility)
  - ❑ Cardiovascular effects (pregnancy induced hypertension)
  - ❑ Cancer* (testicular, kidney)

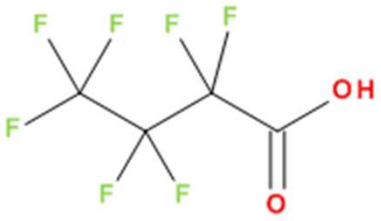
https://pfas-1.itrcweb.org/7-human-and-ecological-health-effects-of-select-pfas/

Spearhead-1951 to 2003 Dupont released 1.7 million pounds PFOA Parkersburg, WV

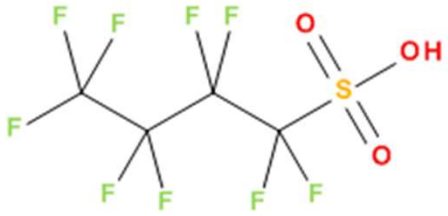
- Snapshot

- Starting in 1998, multiple lawsuits were filed in US courts against chemical company DuPont in relation to PFOA used to produce Teflon. Local farmers, residents and company workers claimed to have suffered illnesses linked to PFOA pollution from DuPont's Parkersburg plant in West Virginia. In one class action lawsuit settled in 2005, DuPont agreed to provide up to $235 million for medical monitoring of over 70,000 people. There have been numerous individual lawsuits from victims of PFOA-related diseases. In February 2017, DuPont settled over 3,550 lawsuits for $671 million.

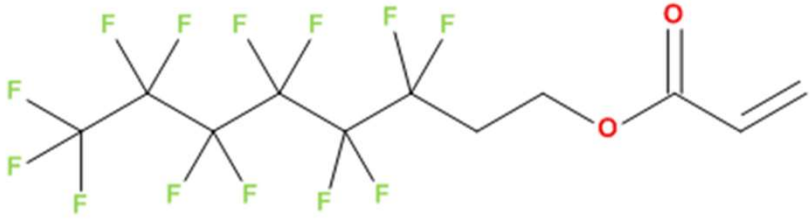
Replacement PFAS



PFBA



PFBS



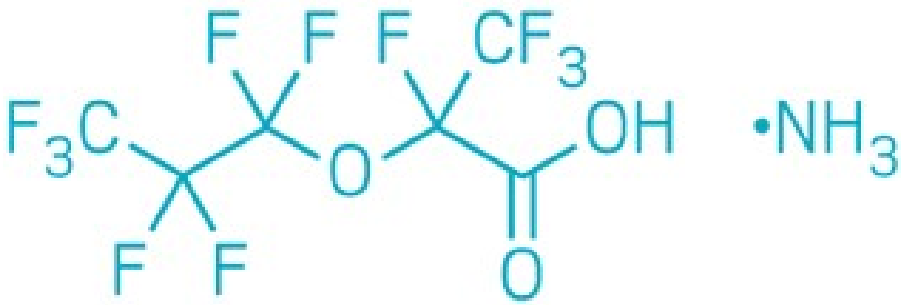
6:2 Fluorotelomer acrylate

- Industry Claims they are safer
- Precursors are still longer chain C8
- PFBA-food packaging and film
- PFBS-surfactants/repellents, metal plating, pesticides, and flame retardants

GenX in the Lower Cape Fear River Basin

AKA HFPO-DA (Dimer Acid)

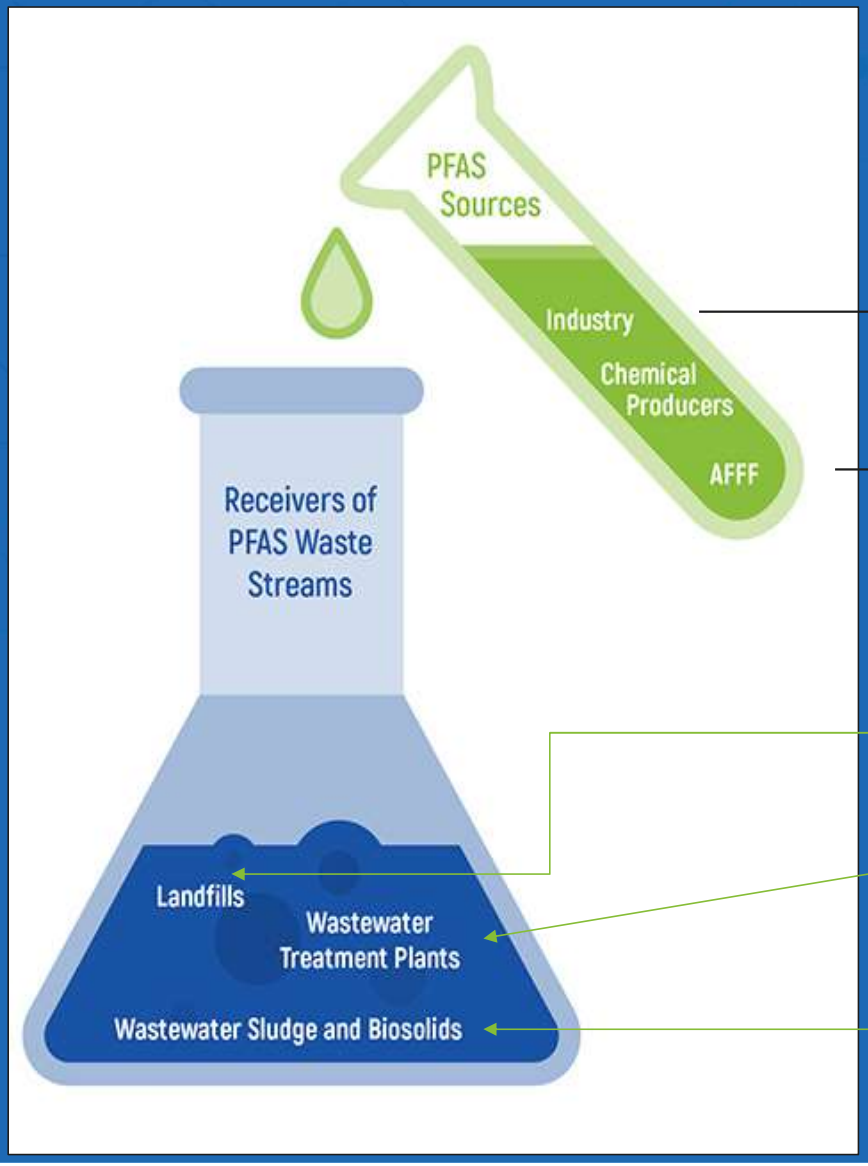
Dupont 2007 as a replacement product for PFOA



GenX

THE PFAS LIFECYCLE

- Industry is the most common source of PFAS contamination - both the manufacturers of PFAS chemicals and those that use them in the products they make.
- PFAS do not degrade naturally, chemicals can remain in the surrounding soil for decades.



- Textile manufacturing
- Certain paper food wrapping
- Metal plating & etching
- Wire manufacturing
- Pesticides
- Personal care products
- Non-stick cookware

Department of Defense and other users of AFFF (Aqueous film forming foam)

Especially if unlined, such as those used for construction and demolition debris

Can covert PFAS precursors into PFOA and other PFAAs

Over half of the sludge produced in the US is land-applied as biosolids and may introduce PFAS into the food chain

Overview

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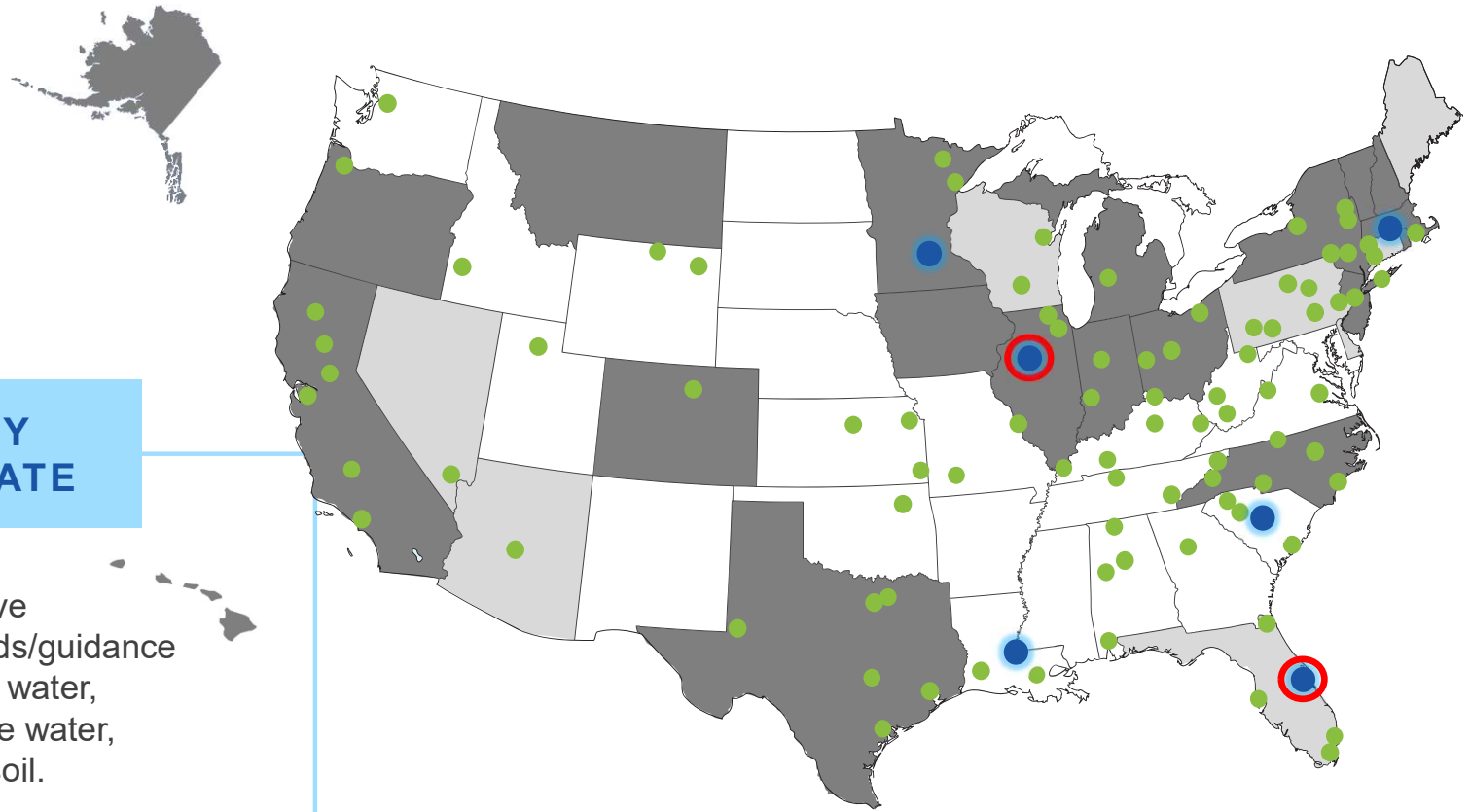
THE PFAS PUZZLE

- Lack of federal regulation
- Non-uniformity of state regulations or test methods
- Lack of environmental test methods
- Ever-changing variety of compound lists and RLs
- Thousands of PFAS compounds
- Expanding variety of analytical matrices
- Low DLs vs. contaminated matrices
- Challenging field sampling protocols

REGULATORY UPDATE: STATE

So far, 25 states have established standards/guidance for PFAS in drinking water, groundwater, surface water, wastewater and/or soil.



PFAS Strategic Roadmap
US EPA's Commitments to Action 2021–2024

RESEARCH

- Invest in R&D
- Increase understanding of PFAS exposures and toxicity, human health and ecological effects, and effective interventions that incorporate the best available science.

RESTRICT

- Pursue a comprehensive approach to proactively prevent PFAS from entering air, land, and water at levels that can adversely impact human health and the environment.

REMEDIATE

- Broaden and accelerate the cleanup of PFAS contamination to protect human health and ecological systems.

REGULATORY UPDATE: FEDERAL

- UCMR 5 finalized December 2022 for the nations Public Water Systems
- Establish a national drinking water MCL PFOA/PFOS (Fall 2022)
- GenX Toxicity report released 25-Oct-21, PFBA, PFHxA, PFHxS, PFNA, and PFDA to follow (Fall 2021, ongoing)
- Propose rule - PFAS chemicals as hazardous substances (Spring 2022)
- Address PFAS air emissions, mitigation, fate and transport (Fall 2022)
- Restrict discharge on industrial releases of PFAS (2022), NPDES (2022)

Which PFAS were addressed in the new Heath Advisories?

- 4 PFAS – PFOA, PFOS, GenX, PFBS
- PFOA and PFOS not in US production

Are GenX and PFBS still in production?

Yes

- GenX, a Chemours product, is the replacement chemical for PFOA in the production of Teflon
- PFBS, a 3M product, is the replacement chemical for PFOS in the production of Scotchgard

Do you think the EPA will lower reporting limits or method detection limits for PFAS in drinking water?

- How do the new Health Advisory levels correlate to current EPA test methods and their detection limits which are higher?
- GenX and PFBS – no problem
- PFOA and PFOS – challenging considerations

Chemical	Lifetime Health Advisory Level, ppt	Minimum Reporting Level, ppt (EPA 533 under UCMR 5)	Typical Lab Reporting Limit, ppt (EPA 533)	Typical Lab Method Detection Limit, ppt (EPA 533)
PFOA	0.004 (Interim)	4	2	0.32
PFOS	0.02 (Interim)	4	2	0.36
GenX	10 (Final)	5	2	0.8
PFBS	2,000 (Final)	3	2	0.44

What's the history of HAs, MCLs, and MCLGs?

- >100 Health Advisories have been issued
- 87 MCLs
- 83 MCLGs – 29 are set at zero, with MCLs set at ppb levels
- Example – Benzene HA-0.003 ppm, MCL-0.005 ppm, MCLG-zero

Source: https://www.epa.gov/system/files/documents/2022-01/dwtable2018.pdf

When do you think the EPA will finalize the MCL for PFOA/PFOS?

- MCLs and MCLGs will be proposed for public comment by Fall 2022
- MCLs and MCLGs will be finalized by Fall 2023

Do you think other PFAS compounds will be included in additional Health Advisories?

- Thousands of PFAS in production
- 29 PFAS included in UCMR 5 with health effects data associated with consumption in water
- EPA has already stated its plans to develop toxicity data for five other PFAS

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UCMR 5 - BACKGROUND

- UCMR was established to monitor unregulated contaminants in drinking water every 5 years
- All large systems serving over 10,000 people are required to monitor
- EPA pays for small systems testing 3,300 to 10,000
- Addition of systems more than doubles the number required to participate to approximately 10,300
- A representative sample is taken from systems serving less than 3,300 people
- UCMR 5 was published in the Federal Registry March 11, 2021

Source: USEPA UCMR 5: https://www.epa.gov/dwucmr/fifth-unregulated-contaminant-monitoring-rule

UCMR 5 - BACKGROUND

Changes from UCMR 4 to UCMR 5

- Addition of all systems that serve 3,300 – 10,000 consumers – compelled by AWIA 2018
- EPA is intent on paying for testing for all systems that serve 3,300 – 10,000 consumers in its "small systems" contract with 800 randomly selected smaller systems, "subject to the availability of appropriations"
- Addition of systems more than doubles the number required to participate to approximately 10,300

UCMR 5 – TESTING & SAMPLING

UCMR 5 contaminants and sampling

- 29 PFAS compounds by EPA 537.1 and EPA 533 – each sample will be required to include 1 Field Reagent Blank per method
- Lithium by EPA 200.7
- Sampling at the Entry Point To the Distribution System (EPTDS, EP, POE) only

UCMR 5 – SAMPLING SCHEDULE

- EPA will assign a 12-month sampling schedule for each system between January 2023 – December 2025
- Groundwater Systems – sample each Entry Point to the Distribution System (EPTDS) – twice during a 12 consecutive month period
- Surface water and Groundwater Under Direct Influence (GWUDI) systems – sample quarterly during a 12 consecutive month period

UCMR 5 – BUDGETARY INFORMATION

- EPA estimates all testing costs per sampling point, per sampling event to be $950
- Contact us for detailed budgetary costs

UCMR 5 – SDWARS

- Safe Drinking Water Accession and Review System (SDWARS) used by PWSs and EPA-approved UCMR 5 laboratories to report results
- Internet-based electronic reporting system that utilizes a secure access portal, the Central Data Exchange (CDX), to access SDWARS 5
- SDWARS 5 user instructions and trainings for labs, PWSs, and States will be available after the final rule is published Fall 2021
- January 2022 EPA issued email to all large PWSs providing direction for actions that must be taken

Source: USEPA SDWARS: https://www.epa.gov/dwucmr/reporting-requirements-unregulated-contaminant-monitoring-rule-ucmr-5

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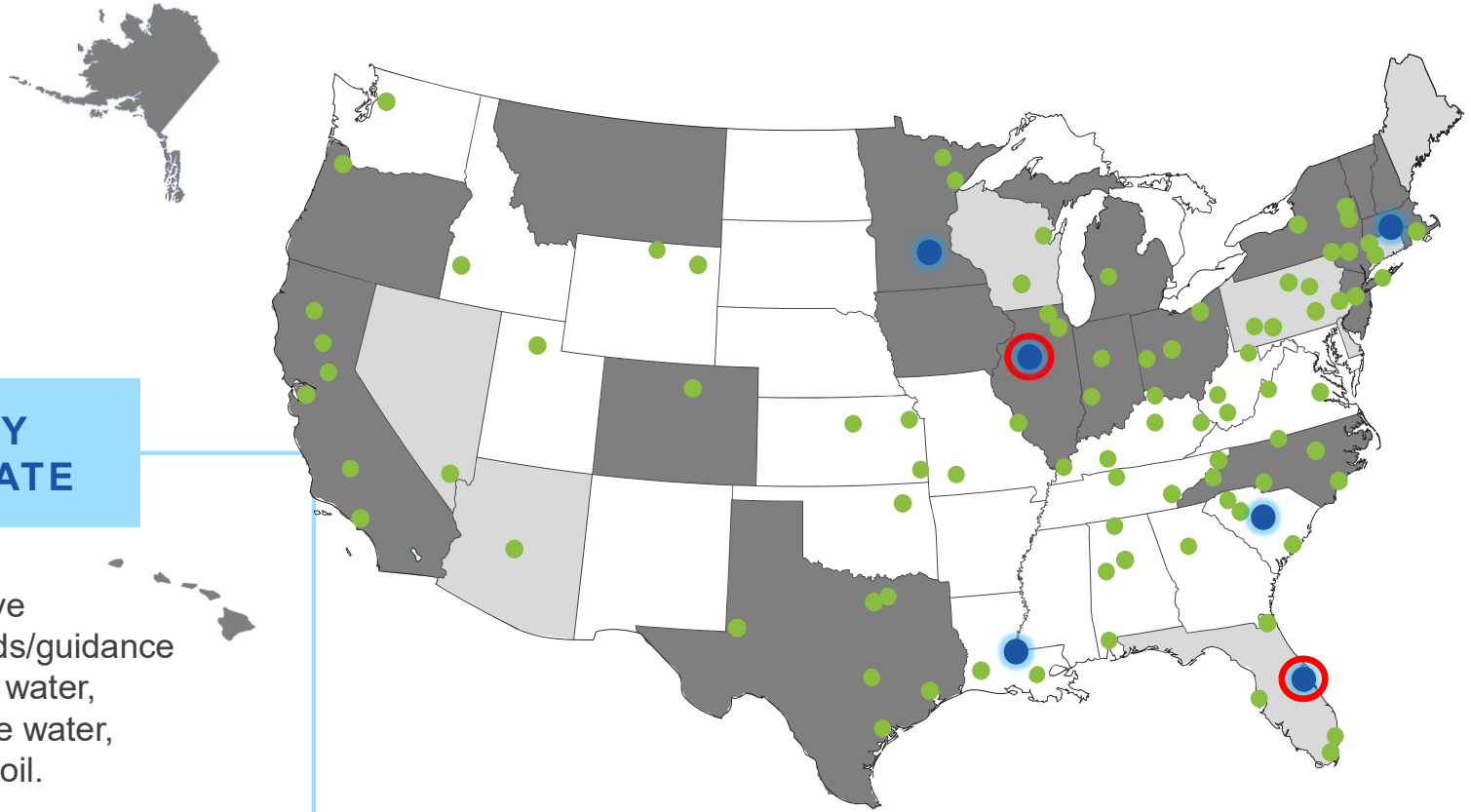


EPA 537.1

- First Published DW Method
- Reports 18 PFAS
- Used for Compliance
- FRB Required
- MS/MSD are part of QC
- Does not use Isotope Dilution

EPA 537.1 (18) DW only	
Acronym	**CAS Number**
PFHxA	307-24-4
PFHpA	375-85-9
PFOA	335-67-1
PFNA	375-95-1
PFDA	335-76-2
PFUnA	2058-94-8
PFDoA	307-55-1
PFTrDA	72629-94-8
PFTA	376-06-7
PFBS	375-73-5
PFHxS	355-46-4
PFOS	1763-23-1
NMeFOSAA	2355-31-9
NEtFOSAA	2991-50-6
HFPO-DA	13252-13-6
ADONA	919005-14-4
9Cl-PF3ONS	756426-58-1
11Cl-PF3OUdS	763051-92-9

EPA 533

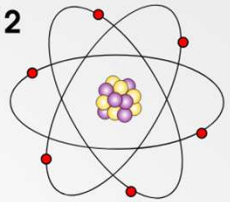
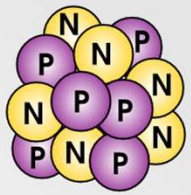
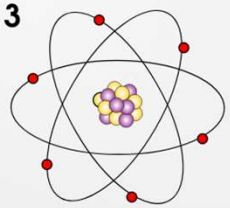
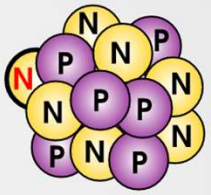
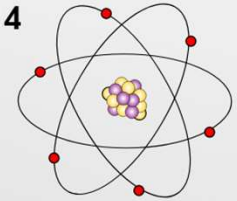
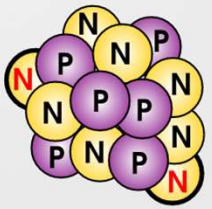
- Uses Isotope Dilution
- Accounts for analyte losses
- 25 PFAS reported
- Addition of source identifiers such as:
  - NFDHA (food packaging)
  - PFEESA (replacement)
  - PFMOPrA (manufacturing)
  - PFMOB (manufacturing)
- Requires FRB
- MS/MSD for QC

Analyte	Analyte
PFBA	PFOS
PFPeA	FTS 4:2
PFHxA	FTS 6:2
PFHpA	FTS 8:2
PFOA	PFMPA
PFNA	PFMBA
PFDA	HFPO-DA
PFUnA	NFDHA
PFDoA	ADONA
PFBS	PFEESA
PFPeS	9Cl-PF3ONS
PFHxS	11Cl-PF3OUdS
PFHpS	

USEPA reports 25 from EPA 533 and 4 that do not overlap from EPA 537.1

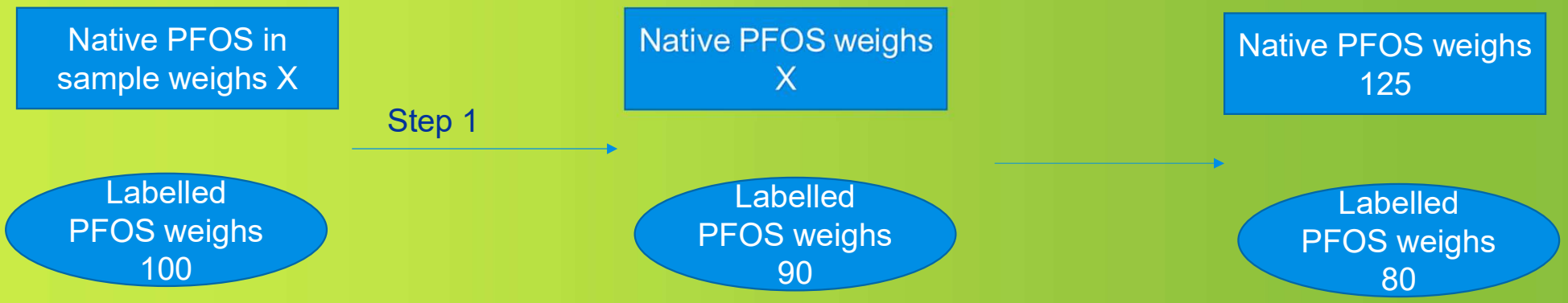
ANALYTE	537.1	533
PFEESA		•
HFPOA-DA/Gen X	•	•
NFDHA		•
PFOS	•	•
PFUdA	•	•
N-MeFOSAA	•	
PFPeA		•
PFPeS		•
6:2 FTS		•
N-EtFOSAA	•	
PFHxA	•	•
PFDoA	•	•
PFOA	•	•
PFDA	•	•
PFHxS	•	•
PFBA		•
PFBS	•	•
PFHpA	•	•
PFHpS		•
PFNA	•	•
PFTeDA	•	
PFMOPrA		•
8:2 FTS		•
PFTrDA	•	
9Cl-PF3PONS	•	•
4:2 FTS		•
11Cl-PF3OUdS	•	•
PFMOBA		•
ADONA	•	•

CARBON ISOTOPES

	Atoms	*Atomic nucleus*	
6 protons + **6** neutrons	C^{12} 		**No** additional neutrons
6 protons + **7** neutrons	C^{13} 		**One** additional neutron
6 protons + **8** neutrons	C^{14} 		**Two** additional neutrons

How does Isotope Dilution Work?

The Chemistry stays the same the only difference is the molecular weight
Note-Example weights are the amount of PFOS in the sample



Solve for X based on ratio
Simplified

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SAMPLING REQUIREMENTS

Why is additional training necessary?

- These items contain PFAS and may contaminate your samples

SAMPLING REQUIREMENTS

Clothing and Hygiene

- No clothing or boots containing Gore-Tex™
- Safety boots must be made from polyurethane or PVC
- No materials containing Tyvek®
- Do not use fabric softener on clothing to be worn in field
- Do not use cosmetics, moisturizers, hand cream, or other related products the day of sampling
- Do not use unauthorized sunscreen or insect repellant
- No Sharpies markers
- Wet weather wear - made of polyurethane and PVC only
- Wash hands and put on powderless nitrile gloves
- No food or drink at the sampling site

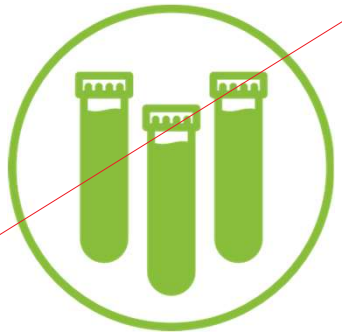
FIELD QC SAMPLES

FIELD REAGENT BLANK (FRB)/ FIELD BLANK (FB)

meant to validate that field sampling activity did not cause sample contamination

EQUIPMENT/ RINSATE BLANK (EB)

meant to validate cleanliness of sampling equipment before sampling and between sampling points



TRIP BLANK (TB)

meant to validate that samples were not cross-contaminated in route to lab

SAMPLING REQUIREMENTS

Sampling Procedure – Container Set Contents

- Container sets will be shipped to you each quarter
- FedEx Ground Delivery

SAMPLING REQUIREMENTS

Sampling Procedure – Check Cooler Contents

- Remove and open large cooler bag that includes:
- Container sets for each POE sampling point in ziplip bags
- Field Reagent Blank sets in ziplip bags
- MS/MSD container sets (at lab's discretion)

SAMPLING REQUIREMENTS

Sampling Procedure – Container Set Contents

- Container order form that itemizes contents - review
- Chain of Custody form – complete this form
- Sampling instructions - review
- Nitrile gloves – put these on after washing hands
- Return sample shipping label – FedEx Standard Overnight for weekday delivery – do not ship on Friday

SAMPLING REQUIREMENTS

Sampling Procedure – Container Set

- Samples-2 X 250 mL 537.1 contains Trizma
- FRB-1 Empty 250 mL 1 PFAS free Water filled 250 mL with Trizma Labelled 537.1
- Samples-2 X 250 mL 533 contains ammonium acetate
- FRB-1 Empty 250 mL 1 PFAS free Water filled 250 mL with ammonium acetate Labelled 533
- MS/MSD if needed will be 2X250 mL labeled by method
- Lithium 2 X 250 mL with Nitric Acid for Samples and one Trip Blank

SAMPLING REQUIREMENTS

Sampling Location

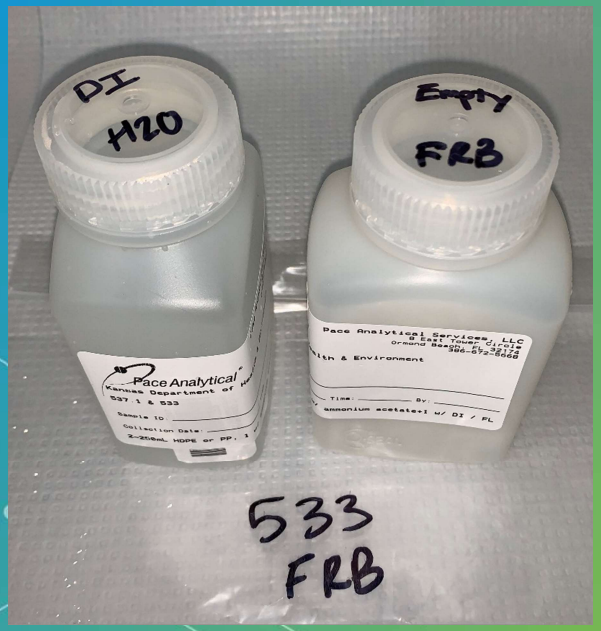
- All samples are to be taken at each Point of Entry to the distribution system
- Prior to sampling open valve and let water run for several minutes
- Slow water flow down to the diameter of a pencil

SAMPLING REQUIREMENTS

Sampling Procedure

- Wash hands and put on nitrile gloves
- Remove container cap and fill to neck one at a time
- Do not place lid face down on any surface
- Fill each sample container set to neck
- Fill each MS/MSD container set (if included) to the neck
- Do not overfill as this will wash out dry chemical preservative
- Open, fill, and close each lid tightly - one container at a time
- Invert each container 5 times to dissolve preservative in water
- Complete info required on container labels
- Return containers to applicable ziplip bags and seal bags

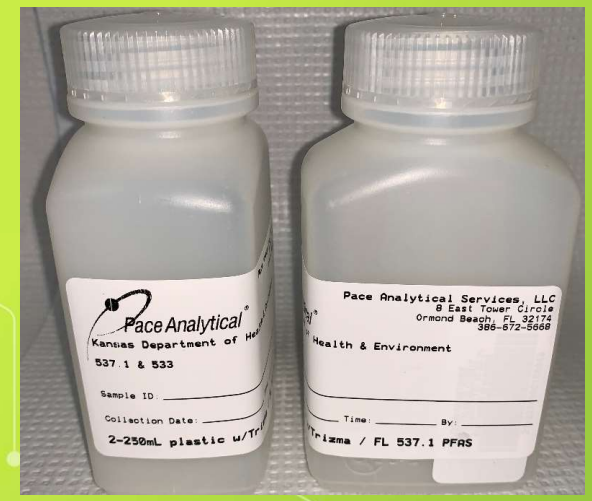
SAMPLING REQUIREMENTS



Sampling Procedure – Field Reagent Blank (FRB)

- 1 FRB per sampling point
- 2 containers filled with PFAS-free DI water
- 2 empty containers
- Purpose of FRB is to verify no cross contamination of samples
- Open containers of DI water
- Open empty containers, do not place lid face down on any surface
- Pour DI water into empty containers
- Close lids tightly
- Invert containers 5 times to dissolve preservative in water
- Complete info required on container labels
- Return containers to applicable ziplip bag and seal bag

SAMPLING REQUIREMENTS



Sampling Procedure – Container Labels

- Record on each container label
- Sample ID – your POE sampling point ID
- Sampling collection date
- Sampling collection time
- By – your initial
- Collection date and time required for holding time purposes – 14 days for EPA 537.1, 28 days for EPA 533

SAMPLING REQUIREMENTS

Repack the Cooler

- Place sealed ziplip bags of samples and FRBs into large cooler liner bag
- Fill large cooler liner bag with ice
- Samples must be received at lab 2-10°C
- If sampling on hot days and POE water is warm – consider keeping samples on ice overnight, drain cooler, and repack with ice
- LOTS of ice

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THANK YOU

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Additional resources:

- PFAS.com
- PACELABS.COM | Search: PFAS